

NOMENCLATURE FOR PYROLYSIS EXPERIMENTS INVOLVING H₂O

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The importance of H₂O in laboratory pyrolysis experiments designed to simulate natural processes is well documented in studies of coalification (Berl and Schmidt, 1932; Schuhmacher et al., 1960) and petroleum formation (Jurg and Eisma, 1964; Lewan et al., 1979). Industrial pyrolysis processes also benefit from the presence of H₂O as demonstrated in oil-shale retorting (Gavin, 1922, p. 181), conversion of coal to oil (Fischer, 1925, p. 180), heavy oil upgrading (McCullum and Quick, 1976a and b), and conversion of organic refuse to oil (Appell et al., 1971 and 1975). As experimental work continues to indicate that the phase as well as the presence of H₂O are important in natural and industrial processes, a nomenclature for pyrolysis experiments involving different H₂O phases is needed to improve interlaboratory communication and comparison of results. The following nomenclature is proposed to meet this need.

Hydrous pyrolysis as originally defined by Lewan and others (1979) denotes experiments in which a sample is pyrolyzed in contact with H₂O liquid. This condition best represents subsiding sedimentary basins in which the pores and fractures in sedimentary rocks are usually filled with water. As shown in Figure 1, the upper temperature limit for pure H₂O in this type of pyrolysis is 374°C, but higher temperature limits in excess of 600°C may be obtained by the addition of soluble salts (i.e., NaCl). H₂O in hydrous pyrolysis experiments typically occurs as both liquid and vapor, unless pressure regulators are employed to maintain only a liquid phase. It is important in the vapor/liquid H₂O system to optimize the amount of water used for specific reactor and sample volumes to insure that the sample is completely submerged in the liquid phase during pyrolysis (Lewan, 1993).

Supercritical H₂O pyrolysis denotes experiments in which a sample is pyrolyzed in contact with a supercritical fluid containing more than 50 mole % H₂O. Although the lower temperature limit for pure water in this type of pyrolysis is 374°C, this critical temperature may be lowered below 300°C with the addition of CO₂ to the system (Figure 1). Supercritical H₂O pyrolysis represents deep crustal regimes where metamorphic grades in excess of greenschist facies occur.

Steam pyrolysis is more difficult to define because sedimentary organic matter and its accompanying rock usually generate or liberate minor amounts of H₂O during experiments commonly referred to as **dry** or **anhydrous pyrolysis**. The headspace in these experiments is typically sufficient for the minor amounts of

evolved H₂O to occur as vapor at a partial pressure dictated by the available volume and experimental temperature. As an operational definition, it is suggested that steam pyrolysis denotes experiments in which a sample is pyrolyzed in contact with H₂O vapor at partial pressures in excess of 20 percent of its saturated vapor pressure at experimental temperatures. Steam pyrolysis represents localized near-surface conditions where geothermal vents or subaerial volcanoes are active.

Hydrous, supercritical H₂O, and steam pyrolysis may be collectively referred to as hydrothermal pyrolysis or aquathermolysis (e.g. Siskin et al., 1990). These collective names are particularly useful for referring to pyrolysis experiments in which insufficient information is given to assess the H₂O phases present or the phase in which a reaction has occurred at experimental conditions.

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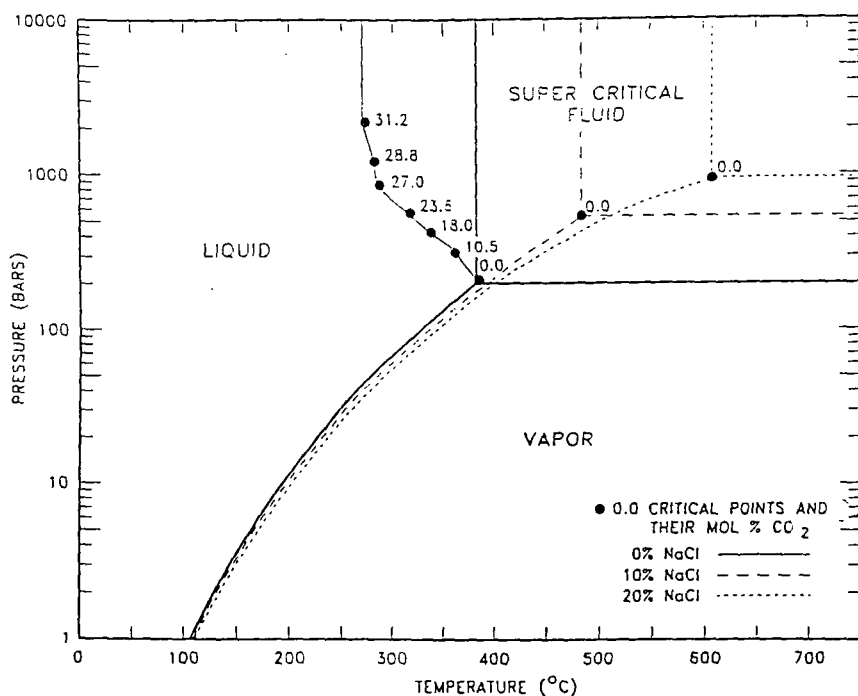


Figure 1. Pressure-temperature diagram showing phase relations and critical points for pure H_2O (heavy solid lines), CO_2 in solution with H_2O (solid circles on light solid line refer to critical points at denoted CO_2 mole fractions), 10 wt% NaCl solution with H_2O (dashed lines), and 20 wt% NaCl solution with H_2O (dotted lines). Diagram is based on experimental data reported by Haas (1976), Sourirajan and Kennedy (1962), and Takenouchi and Kennedy (1964).